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The heats of combustion of a few organic compounds

Orin David Cunningham
The University of Montana

THE HEATS OF COMBUSTION OF A FEW ORGANIC COMPOUNDS.

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ORIN DAVID CUNNINGHAM.

I wish here to express my gratitude to Professor Richard H. Jesse for the interest that he has shown in me and my work.

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HISTORICAL

Thermochemistry during the last half of the 19th Century was centered around three men; and our most important thermochemical data were obtained by these men and their pupils. The most important of these men was Julius Thomsen. His work extended over a period of thirty years. In general it may be said that during that period practically every simple inorganic process was investigated calorimetrically and the heats of combustions of a number of organic compounds were determined. In all he made 3560 calorimetric determinations. His collected works, published in four volumes, comprises the most important thermochemical data on record.

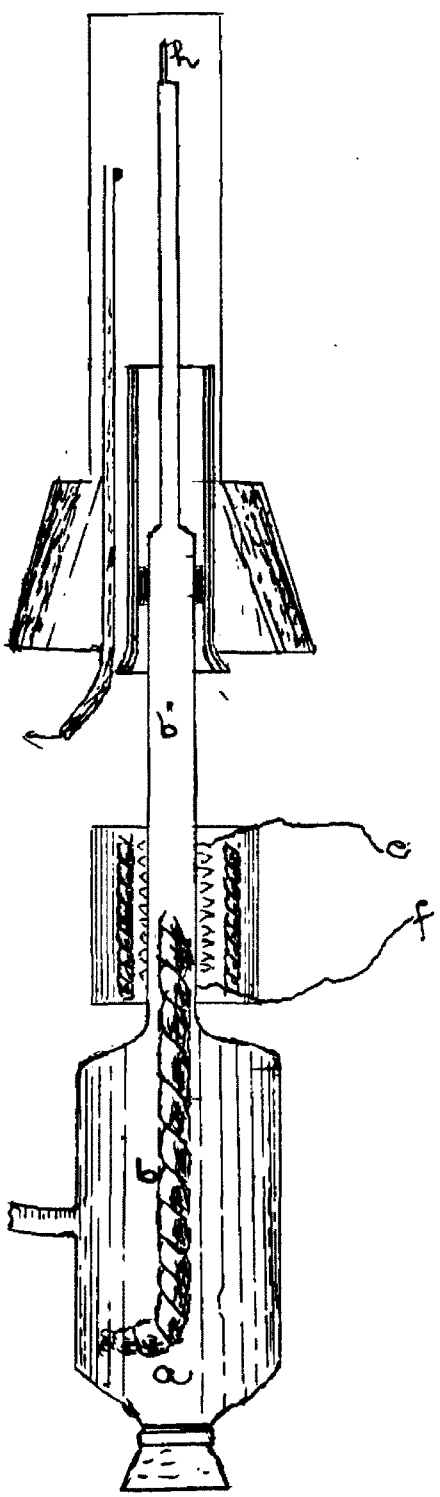
Thomsen's thermochemical work was a direct result of his affinity theory. In his own words he expresses his theory as follows: "The force which unites the component parts of a chemical compound is called affinity. If a compound is split up, whether by the influence of electricity, heat or light, or by the addition of another substance, this affinity must be overcome. A certain force is required the amount of which depends on the strength of the affinity.

If we imagine, on the one side, a compound split up into its component parts and on the other side these parts again united to form the original compound, then we have two opposite processes the beginning and end of which are alike. It is therefore evident that the amount of force required to split up a certain compound must be the same as that which is evolved if the compound in question is again formed from its component parts.

The amount of force evolved by the formation of a compound can be measured in absolute terms; it is equal to the amount of heat evolved by the formation of the compound." It is true that the conception of affinity was known prior to Thomsen but to him belongs the credit of being the first to conceive and carry out experimentally the idea that affinity could be measured quantitatively by estimating the heat evolved in a chemical process.

On the basis of this theory Thomsen sought to obtain clues as to the constitution of organic compounds by comparing their heats of combustion.

The calorimeter that he used for this purpose, Fig. I, was a considerable improvement over any that had been used previously. It will be seen that his form of apparatus permitted the use of organic liquids only. It consisted essentially of a brass calorimeter can (A) of three liters capacity; a platinum lined combustion chamber (a) of 200 c.c. capacity, surrounded by a spiral tube (cc), 1.8 meters long, and 5 m.m. in diameter; and a ebonite insulator (d) which surrounded the calorimeter can. The cover to the calorimeter can was also of ebonite. The opening (b) was for the insertion of the universal burner, shown in Fig. II., intothe combustion chamber. By means of the Universal burner the organic compound being examined was burned. The liquid to be burnt was placed in the small bulb (a), and passed upward by means of a cotton or asbestos wick (b) where it was heated. The heating was acoomplished by passing an electric current through a platinum spiral, the extremeties of which are e & f, which was carefully insulated from the glass tube (b), and the outside to prevent radiation to the calorimeter. The size of theflame at (h) could be kept constant by maintaining a constant flow of current after ebilution of the liquid began. The remainder of



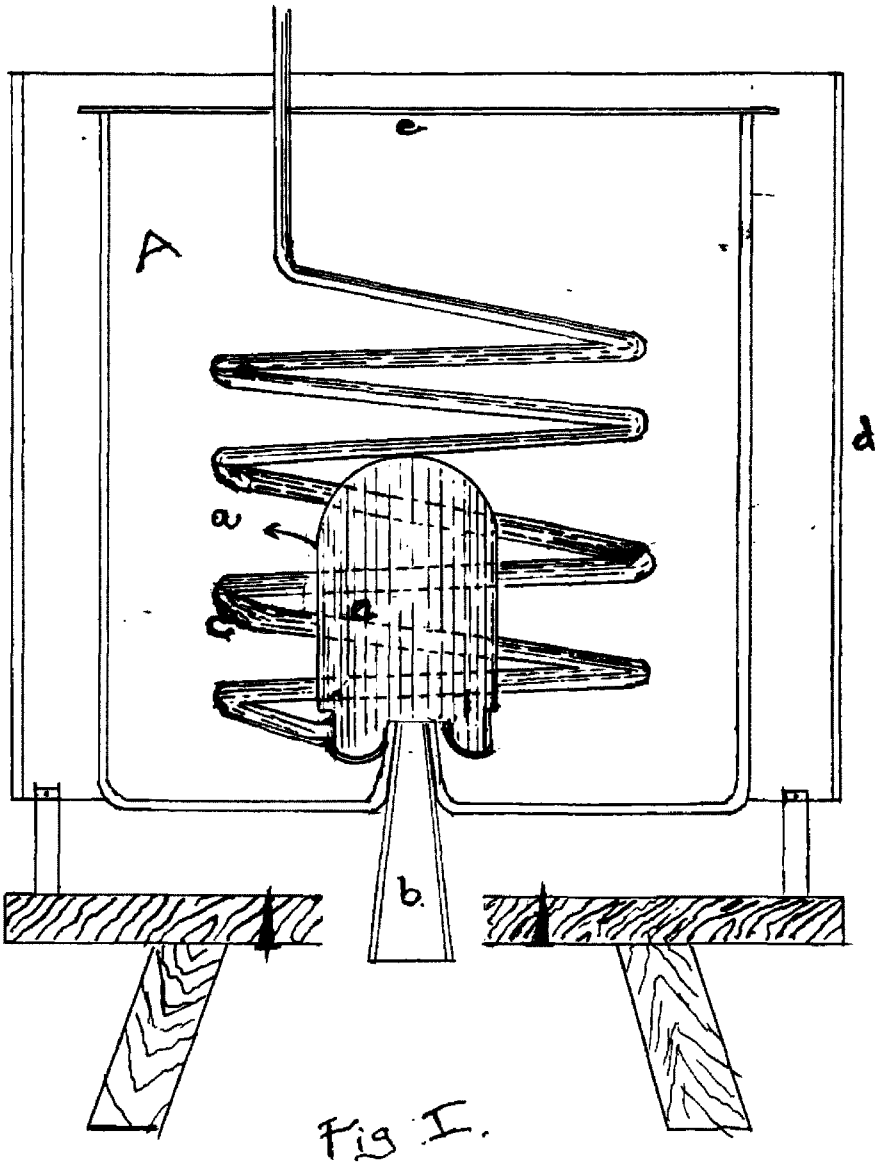


Fig I.

the burner was well insulated so as to prevent any condensation of vapor in its upward passage. The oxygen supply for the combustion of the vapor entered at (1), and was maintained at a constant rate by a suitable device. By means of the burner, it was possible to burn any organic liquid of which the boiling point was not to high. In some cases volitalization was aided by passing an inert gas thru the liquid. This, also, prevented smoky flames.

The gases resulting from the combustion of an organic compound, after passing through the spiral tube within the calorimeter, entered an absorption apparatus. The absorption apparatus consisted of a series of U tubes filled respectively with suitable substances for the absorption of, CO_2, Br_2, Cl_2, and etc. that might be formed during combustion.

The whole calorimetric system, especially the absorption apparatus, offered considerable resistance, which was overcome by means of an aspirator. The aspirator maintained a constant pressure through the whole system, and could be regulated to suit the needs of the experiment.

In an actual experiment, as soon as the combustion of the liquid in the burner was regulated, and the calorimetric system made ready, the lighted burner was inserted in the platinum lined combustion chamber. At the end of an interval of from 10 to 15 minutes the burner was withdrawn. The heat from the burning vapor was transmitted to the calorimeter and measured, while the gases resulting from the combustion were passed thru the absorption apparatus. The amount of substance burned was calculated from the gain in weight of one or more of the absorption tubes. From the data thus obtained it was possible to calculate the heat of combustion of the compound.

It is evident, with our present thermochemical knowledge, that one could not obtain accurate results with such an instrument. His cooling correction was necessarily unsatisfactory, and we now know that this is one of the greatest sources of calorimetric error. By comparing his results with those obtained by our present more accurate methods, there is no doubt that the electric heating device of the universal burner was a source of error in case of the organic liquids with high boiling points, because their heats of combustion are too high in general. The universal burner, also, undoubtedly gave incomplete combustion. The thermometers used at that time were unsatisfactory. There is little evidence as to what the centigrade degree really meant. The determination of heat capacities was, also, not on a very satisfactory basis.

It was stated in the beginning that in recent times three men led the work in thermochemistry. The work of one, a Dane, has just been discussed; the work of the other two, Marcellin Berthellot, a Frenchman, and Stohmann, a German, will now be considered.

Berthellot greatly extended our knowledge in the field of thermochemistry by devising several new forms of apparatus, the most important of which was his oxygen bomb. The bomb, in which combustions were effected under high pressures of oxygen, made it possible to determine the heats of combustion of compounds that could not have been dealt with otherwise.

Berthellot and Stohmann, with the same purpose in view as Thomsen, determined the heats of combustion of a large number of organic compounds, liquids and solids, by means of the oxygen bomb. The apparatus that they used was naturally simpler than the one employed by Thomsen. Cellulose was saturated with the

liquid to be burned. A weighed amount of the liquid in this form was placed in the bomb, and the bomb charged with oxygen under pressure. The bomb was then placed in a calorimeter, and combustion was made to take place at the proper time by fussing an iron wire electrically, which was in contact with the substance to be burned. Although their method was an improvement over Thomsen's, nevertheless it was subject to the same general errors. The presence of an excess of oxygen, they thought, would insure complete combustion. There is no doubt, however, that, in case of the more volitate compounds, there was an incomplete combustion due to evaporation of the liquid.

Thomsen realized before his death that his affinity theory was not strictly true, but in spite of all facts, Berthelot and Stohmann upheld its validity until their dying day. The affinity theory in a practical sense, however, is applicable to the study of the constitution of organic compounds from their heats of combustion, because the free energy change in such a process is not far from the total energy change. One might expect also a similar relationship with respect to the bound energy.

The work of Thomsen, Berthelot, and Stohmann, therefore, failed of a satisfactory outcome, not because of any theoretical fallacies, but because of experimental inaccuracies. Their results showed, however, that there are certain relationships between the members of a homologous series, and unmistakable differences due to variations in structure. Furthermore, the regularities of their results showed that their idea is worthy of further study by more accurate methods.

The revision of thermochemical data for this purpose was begun by E. Fisher and Werde, in Berlin, and Richards, Henderson and Frevert, in Cambridge, about the same time, using somewhat different

methods. The German workers used an electrical resistance thermometer, and the usual method for correcting for radiation. The American workers used a sensitive mercury thermometer, and eliminated radiation corrections by causing the temperature of the environment of the calorimeter to keep pace with the temperature of the calorimeter itself. The two methods gave equally reliable results.

The earlier work at Cambridge was continued by Richards and Jesse. During the earlier part of their work, they used the original form of instrument. Later, however, it was modified somewhat so as to obtain a greater convenience in regulating the temperature of the environment of the calorimeter.

Barry followed Jesse in this work that is being carried on by Richards. The work of Richards and Barry has just recently appeared in publication.

The work is only at its beginning. The principal results of the investigations at Cambridge thus far are:

(1) The efficacy of ~~the adiabatic~~ their method in eliminating all radiation corrections has been established.

(2) A concordance of values has been obtained that indicates an accuracy that is comparably with much quantitative work.

(3) A method of burning organic liquids has been devised that insures complete combustion.

(4) The relative heats of combustion of sugar, benzene, orthoxylene, metaxylene, paraxylene, normal octane, diisobutyl, 2-methyl heptane, 2 4 - dimethyl hexane, 3-ethyl hexane, normal and isopropyl benzene, mesitylene, pseudocumene, and cyclohexane has been obtained.

(5) A striking similarity between the heats of combustion of varies isomers has been noted. Nevertheless, real differences exist, and will doubtless some time, when more data are available, be capable of references to differences in molecular stability and configuration.

The present research consists of an effort to aid in this task of revising our thermochemical data on heats of combustion of organic compounds, so that we can draw conclusions as to their constitution. Our calorimeter is a copy of the one being used at Cambridge.

APPARATUS.

The form of calorimeter originally used by Richards, Henderson, and Frevert is shown in Fig. III. The Calorimeter can (D), in which was immersed the Berthelot combustion bomb, was surrounded below, and on all sides by two cans; one (C) slightly larger than the calorimeter can, nicknamed a "submarine", provided a narrow surrounding air jacket, and the other (A), which was considerably larger than the "submarine", was filled with a caustic soda solution. The top (B) was merely a large pan perforated by several tubes for the admittance of thermometer and stirrer to the calorimeter can, and rested on the outer can. This was also filled with caustic soda solution. By adding sulfuric to the caustic soda solutions the temperature of the environment of the calorimeter could be kept the same as the calorimeter itself.

Such a form of apparatus necessitated the reading of three thermometers (the two thermometers for the caustic soda solutions are not shown in the accompanying drawing), and the manipulation of two burettes besides numerous other minor things. Since, at combustion the calorimeter rose rapidly thru a change of temperature or about two degrees, rapid manipulative work was

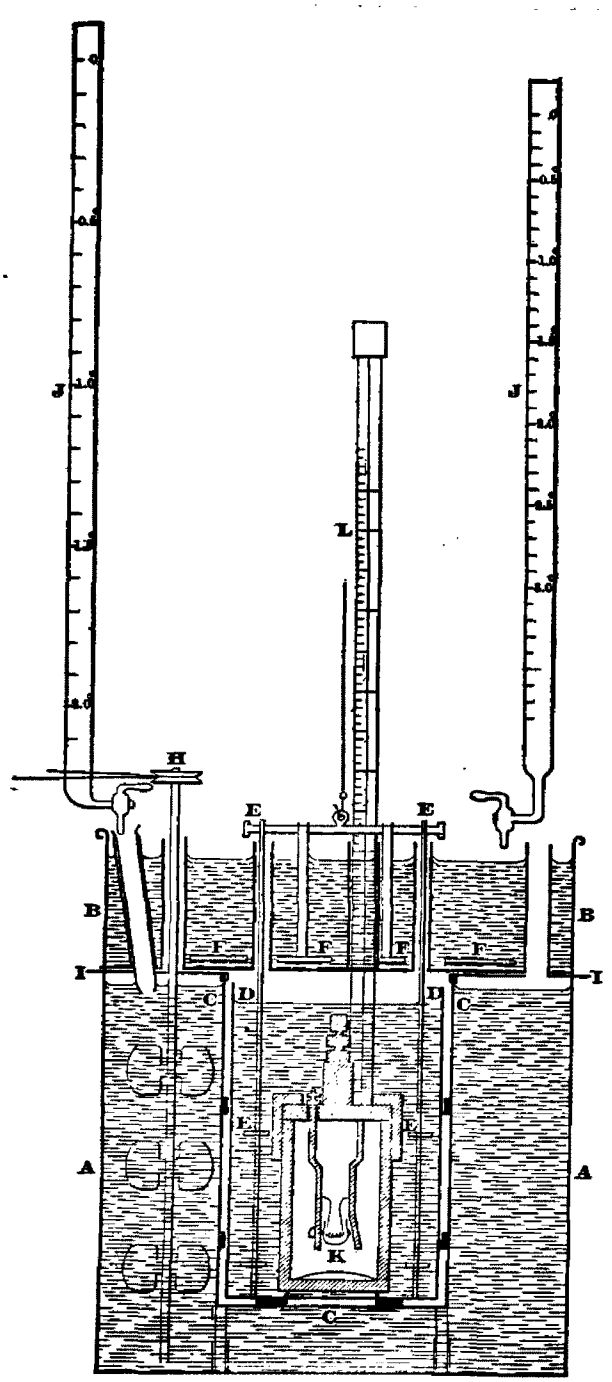


Fig. III

A. Outer vessel. B. Covering vessel. C. Nickel-plated copper can. D. Silver calorimeter. E. Stirrer for calorimeter. F. Stirrer for covering vessel. H. Stirrer for outer vessel. I. Copper cover. J. Burettes. L. Crucible containing substance to be burned. L. Thermometer.

Fig III

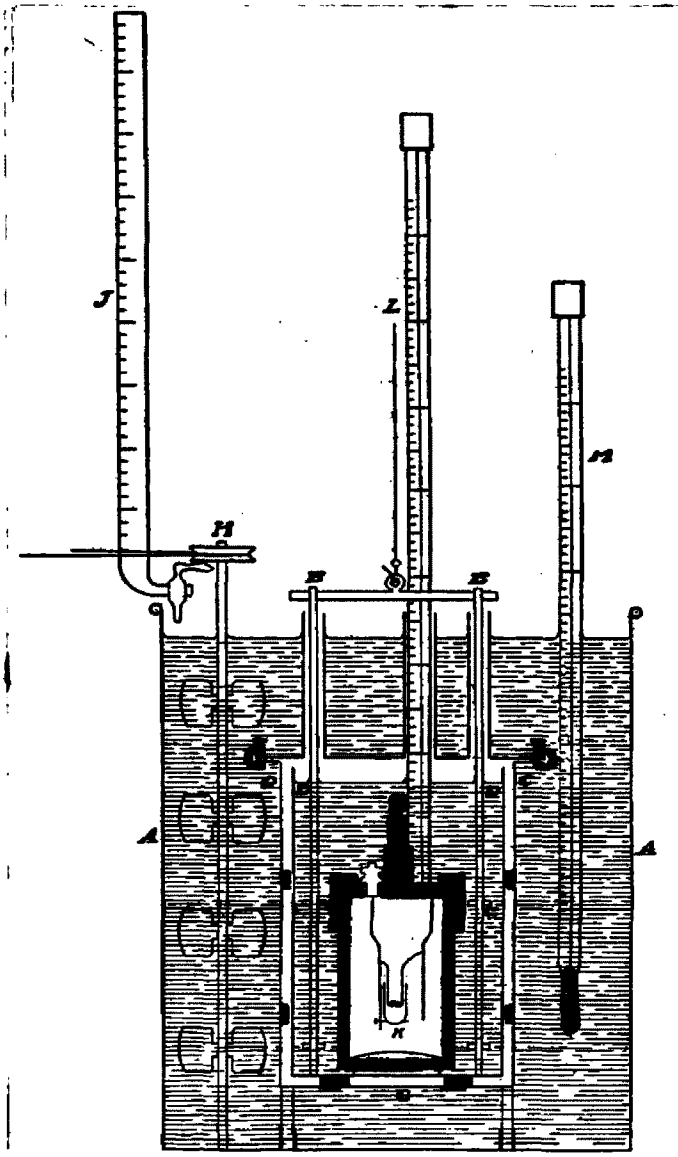


Fig IV

Fig. 2.
Vertical Section.

A. Outer vessel.
C. Nickel-plated copper can.
D. Silver calorimeter.
E. Stirrer for calorimeter.
H. Stirrer for outer vessel.
J. Burette.
K. Crucible containing substance to be burned.
L. Thermometer for calorimeter.
M. Thermometer for outer vessel.

required. It was in view of this that Richards, and Jesse modified the jacketing of the calorimeter somewhat.

The form of calorimeter finally adopted, and the one used in this work, is shown in Fig. IV. The modified form of jacketing did away with one thermometer and one burette, which greatly increased the convenience of experimenting.

A brief description of the construction of the apparatus used in this work will be given. All cans were made of copper and with the exception of the calorimeter can (D) all joints were brazed, since a caustic solution attacks solder. The calorimeter can was soldered, and nickel-plated on the outside. To the upper edge of the can (C) was brazed a circular projecting flange of copper, and to the under edge of this was rivited a circular quarter inch square brass rod. The cover to this can consisted of a circular piece of sheet copper, and bore three tubes for the calorimeter stirrer and thermometer. To the upper edge of the cover was riveted a brass ring similar to the one riveted to the flange. By separating the two brass rings, in the manner shown, from the main body of the can all possible thermal lag of the heavier mass of metal did not effect the calorimeter. For this same reason, the same size of copper sheeting was used in making all parts of the two inner vessels, and the covers. The vessel (C) was made air tight by placing a rubber greased gasket between the flange, and the outer edge of the cover, and clamping the cover to the can by means of six or eight small screw clamps, the pressure of the clamps being borne by the two brass rings. By means of three legs, made of copper tubes, the vessel (C) and its contents were supported, thus allowing for a proper circulation of caustic solution beneath. The can was made stationary by placing the legs in pockets fastened

to the bottoms of the outer jacketing can. The stirrer (E) for the calorimeter was of the reciprocating type, consisting of two perforated rings attached to two slendor supporting rods. Metallic caps were screwed onto the tubes of the calorimeter cover for the passage of the stirrer arms, which contained holes just large enough for the passage of the rods. This prevented the rods from drawing air into the calorimeter during their reciprocating motion, which would cause a cooling of the calorimeter due to circulation of air within. The jacketing can (A) was made of fairly heavy copper sheeting. The caustic solution was circulated by means of the stirrer (H).

The calorimeter can (A), as has been mentioned, was a soldered copper can nickel-plated on the outside. It weighed 1805 gms. and had a capacity of 4000 cc. It was insulated from the can (C) by means of pieces of cork and between the two cans, bottom and sides, there was an air space of 5 m.m.

The bomb used is a modification of the Berthelot bomb put out by the Standard Calorimeter Company. A cross section of it is shown in Fig. V.

There are several distinct features between this bomb and the usual platinum and enamel lined bombs employed for accurate calorimetric work:

(1) The substitution of an alloy, resistant to the action of acids, for the platinum and enamel linings. The main body of the bomb is made of an alloy casting of nickel, copper, tungsten and chromium with small amounts of manganese, aluminum, titanium, boron, and silicon.

(2) The replacement of lead gaskets by well protected rubber gaskets. The cover of the bomb is so made that the shoulder (AA), when the lid is in position, fits tightly against the wall

Fig V

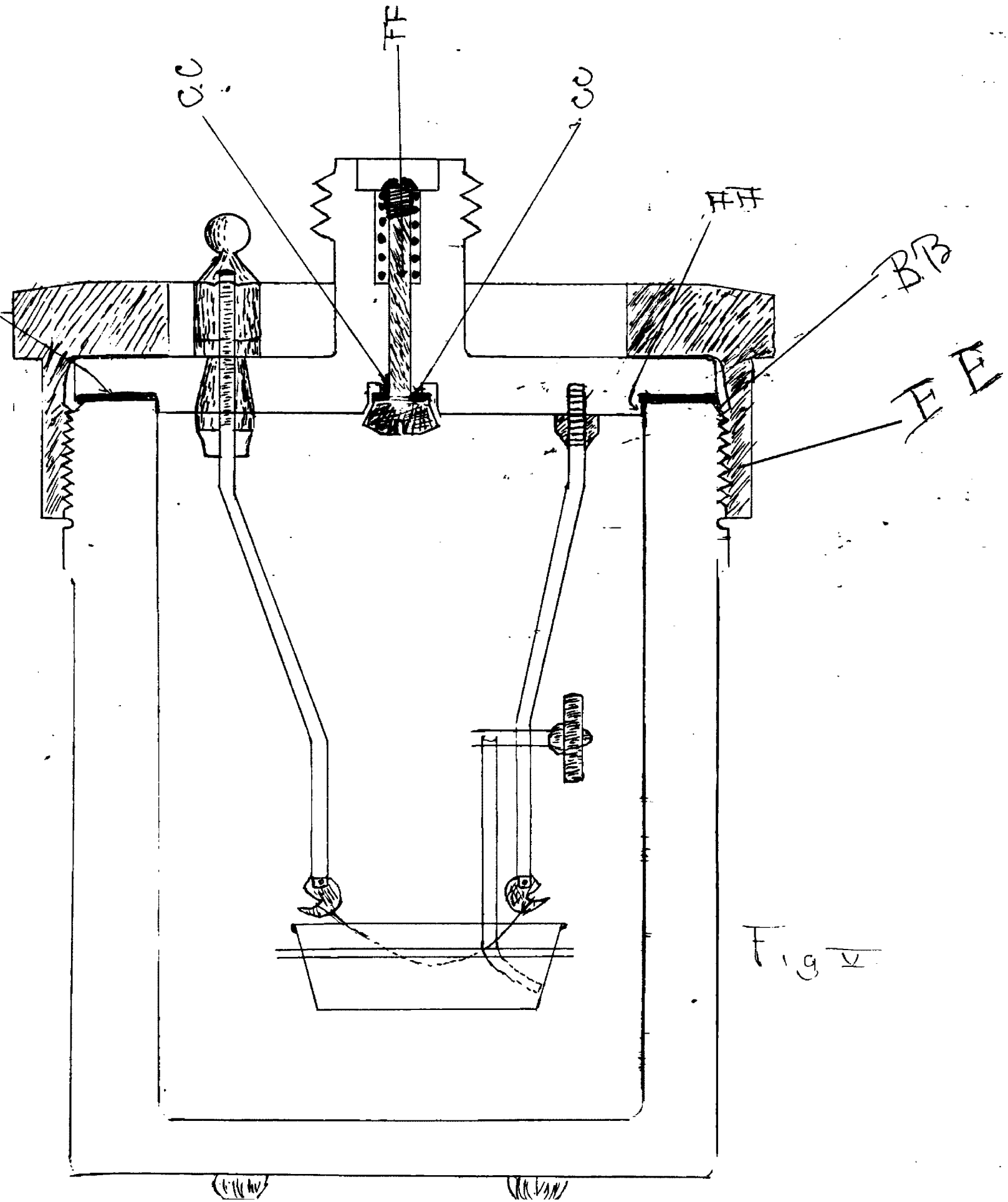


Fig V

of the bomb for a distance of about 3 m.m. The space between the wall of the bomb and the shoulder is machined to a 1/25 of a m.m. The beveled edge of the bomb wall (BB) forms a free space to allow for expansion of the rubber gasket (DD), when the cap (EE) is screwed down, thus preventing any of the rubber gasket from being forced down between the shoulder and the wall. In this manner the rubber gasket is well protected, in a practical sense, from any corrosion that might result from the heat of combustion and gases formed.

(3) The use of a seated valve (FF) bearing a rubber gasket (GG) instead of the troublesome steel needle valve. The rubber gasket of the valve is protected in a manner analogous to that of the other gasket.

Dr. Jesse tested the first successful casting of this bomb at the University of Illinois. He employed a calorimeter for this purpose similar to ours. During this work, he made a series of acid corrosion tests, in which the washings from eight combustions made on sugar and benzoic acid were combined, and analysed quantitatively for copper and nickel. The results obtained showed that the heat evolved by the solution of the alloy during a combustion was within the limits of error. Since these tests were made under conditions analogous to ours, the results are all the more applicable to our work. Besides, slight modifications have recently been made in the composition of the alloy which have probably increased its acid resistance.

The bomb has not as yet been used extensively for accurate calorimetric work. However, the results obtained in this work and, also, those obtained by Dr. Jesse at the University of Illinois in 1912, indicate that it is adaptable for such purposes. If it can be made to give results comparable to those obtained

by the other types of bombs, there is no question of its superiority. It is cheaper; the method of sealing is simpler; and there is no troublesome lining.

The shallow alloy crucible which came with the bomb was replaced by a platinum crucible weighing about six grams. A platinum crucible has several advantages over the shallow dish, especially in the combustion of organic liquids. A deeper dish prevents probably projection of material at time of explosion, and concentrates the heat of combustion, thus insuring a more complete burning of material.

The calorimeter thermometer was a Beckman type and was had been calibrated by the Bureau of Standards. The jacket thermometer was also of the same type, but unstandarized.

The water-equivalent of our calorimeter was determined by the relative method. Sugar was used as a standard and 3945 Calories per gram was accepted as its heat of combustion. It was found that a gram of sugar caused a rise of 1.1301° in our calorimeter. Therefore the water equivalent of our system was $\frac{3945}{1.1301} = 3491$ c.c.

THE COMBUSTION OF SUGAR AND BENZOIC ACID.

The sugar was obtained from the Bureau of Standards. Its heat of combustion was given as 3945 calories per gram.

The details of combustion of the sugar will serve to illustrate the general method used in all combustions. About two grams of granulated sugar was weighed into the platinum crucible, and the crucible then placed in its support. As is shown in Fig. V., this support consisted of an alloy ring fastened to a rod of the same material in electrical connection with, and projecting downward from the bomb cover. Between this rod and a similar one,

insulated from the bomb, was fastened a coil of iron wire which dipped into the sugar. Care had to be taken not to submerge the coil too deep into the sugar or combustion would fail. This was due to the fact that sugar, when under a high pressure and in the presence of water as it finally was in the work, is quite hydroscopic. Too much of the wet sugar in contact with the coil of wire prevented the fusion of the wire within the body of the sugar. The iron wire in every case would fuse down to the sugar, charr the sugar a little, and then stop. In order to avoid a correction for the heat of evaporation of the water formed during combustion, one cubic centimeter of water was added to the bomb chamber. The different parts of the bomb were then placed together, and the bomb charged with 35 atmospheres of oxygen.

The oxygen used was supplied by the Linde Air Products Company of Niagara. It had been obtained from liquid air.

Three thousand grams of water, brought to a temperature from 19°-20° C., was weighed into the calorimeter can. The can was then placed in the "submarine", the intermediate can, and the bomb and the stirrer were lifted into the water. The bomb, by a suitable arrangement, always occupied a central position of the can. This was necessary in order to prevent any possibility of the stirrer striking the projections on the bomb. The cover of the calorimeter was then clamped on, and the whole thing lifted into the jacketing can containing the caustic solution. Sufficient caustic solution was added to completely submerge the calorimeter, and its temperature brought within the neighborhood of that within the calorimeter. After comparing the setting of the two Beckman thermometers, they were placed in their respective places. Electrical and stirring connections were then made. The stirrers were started and the temperatures of the calorimeter

and jacket were adjusted to within 0.01°. Readings were made every minute, the temperature of calorimeter being read to a .001° by means of a magnifying glass, and that of the jacket to a 0.01°. The calorimeter thermometer was tapped at each reading in order to prevent lagging of the mercury thread. As soon as the readings became constant a switch was turned, causing a fusion of the iron wire, and a combustion of the sugar. The current for the fusion of the iron wire was obtained directly from the city line circuit in conjunction with a lamp-bank. As soon as the lamp-bank indicated a fusion of the iron wire the switch was again turned. During the first rapid rise, the temperature of the jacket was kept from 0.05° to 0.10° higher than that of the calorimeter. This was done in order to give sufficient time for complete distribution of the heat in the jacket. After the first three minutes the rise was nearly complete, and the temperatures were adjusted to within 0.01° or 0.02°. Finally the temperatures were made the same. The rise was generally complete in about ten minutes. Readings were made until there was a constant change of temperature.

The calorimeter stirrer made about 78-82 strokes per minute. Stirring corrections for a while were obtained by continuing the thermometric readings of an experiment over a period of 15-20 minutes after the rise in temperature following a combustion had become constant. The corrections thus ~~obtained~~ found were later tabulated, and an average stirring correction was obtained, and used for the experiments that followed. The data from which an average stirring correction was obtained is given below:

No. of the Experiment	Duration of Stirring	Temperature Change	Temperature Change per minute.
#25	18 min.	.006°	.000333°
26	17	.005	.000294
27	15	.004	.000266
28	18	.005	.000277
30	19	.006	.000315
31	20	.007	.000350
32	16	.005	.000312
33	14	.005	.000357
35	12	.004	.000333
36	17	.006	.000353
37	16	.006	.000375
38	13	.004	.000307
		AVERAGE -	.0003226°

The widest discrepancy from the mean is only about ± .0006°. Since on the average there was a rise of 2.6° in the calorimeter during a combustion, this would mean a possible error of .03% for an interval of ten minutes, which in general was sufficient time for an experiment. An error of .03% is within the limits of experimental accuracy.

The jacket stirrer made in the neighborhood of 300 revolutions per minute. This rate of stirring was found to distribute the acid evenly in from 5-7 seconds.

Fifteen centimeters of iron wire, weighing .020 grams, were used. The water equivalent of the system having been about 3491, the rise of temperature in the calorimeter, due to the combustion of one centimeter of wire as calculated from the heat of combustion of iron to magnetic iron, amounted to .000672°.

This was verified by five experiments in which 15 cm. of wire alone were burned. The results obtained are given below.

No. of Experiment*	Length of Wire burned,	Total Change of Temperature.	Change of Temp. per Centimeter.
#1	15 cm.	.011°	.0007333°
2	15	.011	.0007333
5	14.3	.0107	.000612
6	14.7	.009	.000660
7	15	.010	.000747
		AVERAGE - - - -	.000697

The agreement between the experimental value and the theoretical value is as close as could be expected. The value .000697° per centimeter, which was used as a correction, made a total correction of .0104° for 15 cm. of wire.

After the run, the gas was let out of the bomb and the interior examined for carbonacious material, and other indications of incomplete combustion. In working with liquids, the odor of the issuing gas was noted, also. All experiments, of course, were discarded, which gave any indications of incomplete combustion.

The nitric acid formed during the combustion was washed out of the bomb and titrated with sodium carbonate solution. The sodium carbonate solution was made of such a strength, that and acidity equal to one cubic centimeter of the alkali indicated a quantity of nitric acid whose heat of formation must have raised the temperature of the calorimeter .001° The standardization of the solution was effected by Thomsen's equation:

* Experiments #3 and #4 were unsatisfactory and rejected.

$2N + 5O + H_2O + Aq = 2HNO_3Aq + 29.8$ cals.

The following tables records the results on sugar and benzoic acid. The benzoic acid was burnt in the form of pellets. Otherwise the method of combustion was the same as for sugar. It was obtained from the Bureau of Standards.

Experiment	Weight of Sugar	Obs. rise of temperature cor. for bore and emergent stem.	Correction for Stirring.	Correction for iron burnt.	Correction for Nitric Acid.	Correct temperature change.	Temperature change for one gram of sugar.
24	1.8228	2.0793°	-.004°	-.010°	-.003°	2.0621°	1.132°
5	1.68865	1.9275	.006	.009	.003	1.9097	1.131
7	1.7981	2.0533	.005	.010	.003	2.0349	1.132
8	1.7410	1.9858	.004	.010	.003	1.9686	1.130
9	2.0644	2.3563	.006	.010	.003	2.3365	1.132
0	2.0020	2.2825	.006	.010	.003	2.2627	1.130
1	1.7182	1.9651	.007	.010	.003	1.9448	1.132
2	1.9017	2.1694	.006	.010	.003	2.1495	1.130

AVERAGE - - - - - - - - - - - - - - - 1.1311°

erage rise per gram of sugar (weighed in air) = 1.1311°

erage rise per gram of sugar (weighed in vacuo) = 1.1301°

Exp. No.	Weight of Benzoic Acid.	Obs. rise of Temperature Corr for bore and emergent stem	Corr. for Stirring	Corr. for iron burnt	Corr. for Nitric Acid.	Correct Temperature change.	Temperature Change for one gram of Sugar.
#1	1.1681	2.1343°	-.005°	-.010°	-.003°	2.1163°	1.812°
2	1.3201	2.4123	.006	.010	.004	2.3923	1.813
3	1.0181	1.8644	.005	.010	.004	1.8458	1.813
4	1.1354	2.0743	.003	.009	.004	2.0589	1.814
5	1.1426	2.0908	.005	.010	.003	2.0724	1.814
7	0.9101	1.6672	.005	.010	.002	1.6499	1.813
8	0.9438	1.7287	.005	.010	.002	1.7287	1.813
9	0.9459	1.7296	.004	.009	.003	1.7133	1.811
10	0.9366	1.7185	.007	.010	.002	1.6989	1.814

AVERAGE - - - - - - - - - - - 1.8130°

Average rise per gram of benzoic acid (weighed in air) = 1.8130°

Average rise per gram of benzoic acid (weighed in vacua)= 1.8116°

Experiments #10 to #24 were made with oxygen that contained combustible gases, probably Hydrogen since it was made by the electrolysis of water.

The average rise in temperature in this calorimetric system due to the combustion of one gram (weighed in vacuo) of sugar and benzoic acid is thus 1.1301° and 1.8116°, respectively. The greatest deviation of the experimental results from the mean is ±0.09% for sugar, and ±0.1% for benzoic acid. Such errors could easily be made by inaccurate reading of the thermometer. With a scale divided to 1/100°, it would be possible to make an error of .001°, even with a good magnifying glass. This error made in the same direction at the two extreme readings would cancel each other. Should it be made in opposite directions, and error of .002° would result and in a temperature rise of 2.0° this would mean a percentage error of .1%. The average results should be more accurate than this, however.

According to the results obtained for sugar and benzoic acid, a gram of benzoic acid yields $\frac{1.8116}{1.1301}$ = 1.6031 times as much heat on combustion as a gram of sugar. The most recent ratio found by the Bureau of Standards is 1.6020. The agreement here is quite satisfactory. Dr. Jesse at Illinois University obtained the value 1.6014. The ratio for our four highest results of sugar and the average of benzoic acid is 1.6017.

THE COMBUSTION OF BENZENE

The benzene was made from Kahlbaums "thiophenfrei" material. It was first shaken with two successive portions of clean mercury. The second shaking showed no appreciable darkening of the mercury. The benzene was then shaken with four successive quantities (200-300 c.c.) of C. P. concentrated sulfuric acid. The sulfuric turned a yellow, the depth of the color lessening

for each shaking. In order to free the benzene of all traces of acid, it was alternately washed with several portions of water and sodium hydroxide. Following this came several more shakings with mercury. A considerable blackening of the mercury was observed. The shakings were continued until the blackening of the mercury was slight. After washing several more times with water, the benzene was dried over calcium chloride and distilled. The accepted portion of the benzene was then still further purified by crystallization.

The benzene to be burned was placed in thin glass bulbs flattened on both sides, and sealed off in such a manner that the bulb was completely filled. Such a shaped bulb of benzene was able to withstand a pressure of 35 atmospheres without bursting. The bulbs were filled by alternate cooling and heating in cold and hot water. The filling had to be manipulated very carefully in order to avoid a bursting of the bulb. If the bulb was immersed in the hot water to rapidly, it caused an explosive evaporation of the benzene, and a consequent bursting of the bulb. The air within the bulb was displaced not by one or two heatings and coolings, but by many. This was found to be very essential. The bulbs were finally sealed off at room temperature by means of a blow-torch. The following drawings show the bulb in various stages of development.

Fig-1.

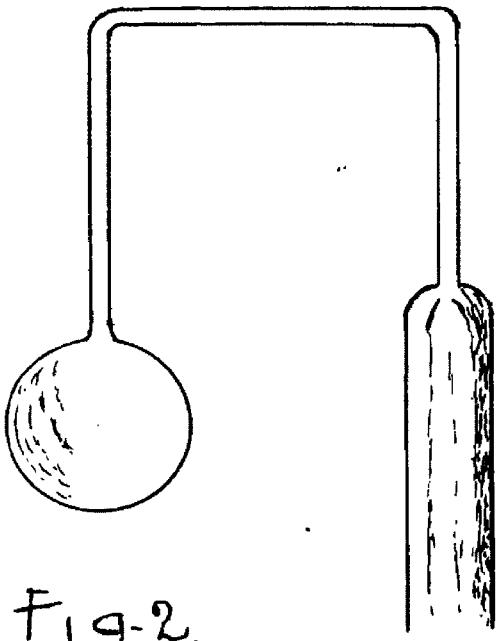


Fig-2.

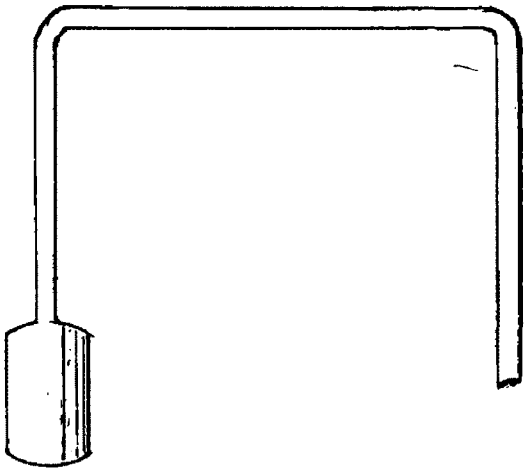


Fig-3.

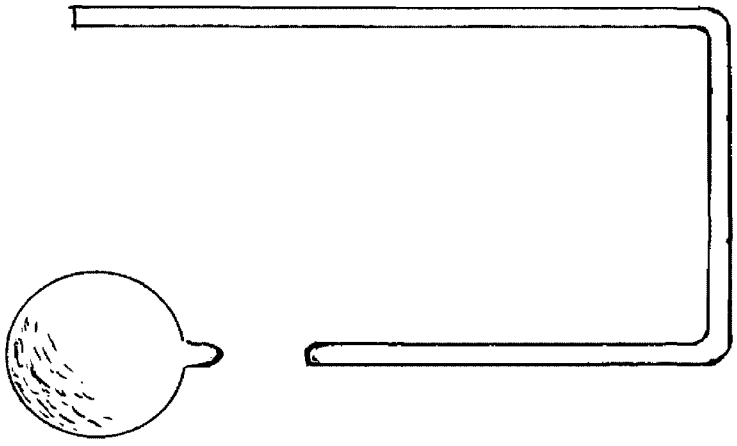


Fig-4.

The bulb of benzene was placed in the bottom of the platinum crucible. A few millimeters above the bulb was placed a narrow thin glass platform made from microscopic slides upon which was placed a weighed pellet of sugar. The coil of wire was placed in contact with the sugar. The fusion of iron wire ignited the sugar, which in turn caused the bulb to break, and an ignition of the benzene at a moment when the top of the crucible was filled with the flames from the burning sugar. Thus no benzene was allowed to escape combustion.

The remainder of the procedure for burning the benzene was the same as that employed for sugar.

The following table is a record of our work on the combustion of benzene:

Exp. No.	Weight of Benzene	Obs. rise of Temp. corr. for bore and emergent stem.	Weight of the Sugar Pellet	Corr. for Sugar	Corr. for Stirring, wire & Nitric Acid	Correct Temperature Change	Temp. Change for one gram of Benzene
#33	.5180	1.6123	.0960	-.1086°	-.019°	1.4851°	2.867°
35	.5739	1.7440	.0712	.0806	.017	1.6459	2.868
36	.6422	1.9754	.1006	.1138	.018	1.8434	2.871
38	.7137	2.1994	.1185	.1341	.016	2.0493	2.871
39	.8564	2.6758	.1711	.1936	.020	2.4621	2.875
40	.6420	2.0423	.1730	.1958	.018	1.8465	2.875
41	.5137	1.6386	.1309	.1481	.016	1.4745	2.871
42	.4731	1.5102	.1205	.1364	.018	1.3563	2.867
					AVERAGE - - - - - - - - - -		2.8706°

Average rise per gram of benzene (weighed in air) = 2.8706°

Average rise per gram of benzene (weighed in vacuo) = 2.8671°

Thus the burning of one gram of benzene causes an average rise of 2.8671° in this calorimetric system. The greatest deviation from the mean is .0004° or less than .02%, which is somewhat greater than the deviations for sugar and benzoic acid. This, however, would be expected, since there is greater opportunity for an incomplete combustion.

The ratio of benzene to sugar is $\frac{2.8671}{1.1301}$ = 2.5371. Similar ratios which have been found at Cambridge are given below:

Richards, Henderson & Frevert - - - - - - - - - - 2.532

Richards & Jesse - - - - - - - - - - - - - - - - - 2.5372

Richards & Davis (University of Manitoba) - - - - 2.5395

Richards & Barry - - - - - - - - - - - - - - - - - 2.533

Richards, Henderson and Frevert had some difficulty with the combustion of benzol, so that their ratio is not entirely satisfactory. Otherwise, our ratio agrees very well with the exception of the one obtained by Richards and Barry.

THE COMBUSTION OF THREE ISOMERIC COMPOUNDS; ETHYL PROPIONATE, METHYL BUTYRATE, METHYL-ISO-BUTYRATE. (R.&J.)

The method of burning the ethyl propionate and methyl butyrate was the same as that employed for benzene. The following is a record of the work done on these two substances.

Exp. No.	Weight of Methyl Butyrate *	Obs. rise of Temperature Corr. for bore and emergent stem	Weight of Sugar Pellet	Corr. for Sugar	Corr. for Stirring, Wire, & Acid	Correct Temperature Rise	Temperature Change for one gram of methyl butyrate
#49	.7240	1.4958°	-.1416	-.1602°	-.017°	1.3191°	1.822°
50	.7157	1.4961	.1548	.1750	.018	1.3036	1.821
51	.8377	1.7034	.1436	.1625	.016	1.5254	1.821
					AVERAGE - - - - - - - - - -		1.8213°

Average rise per gram of methyl butyrate (weighed in air) = 1.8213°

Average rise per gram of methyl butyrate (weighed in vacuo)= 1.8191°

The average rise of temperature for the combustion of one gram of Ethyl propionate, and methyl butyrate in our calorimetric system was thus 1.9348°, and 1.8213°, respectively. Accordingly, a gram of ethyl propionate, and methyl butyrate evolve respectively $\frac{1.9348}{1.3101} = 1.7120$, and $\frac{1.8191}{1.1301} = 1.6196$ times as much heat on combustion as a gram of sugar.

We intended to determine the heat of combustion of methyl-iso-butyrate, but were unable to obtain any. Richards and Jesse did some work on the combustion of this compound. They were not entirely sure of its purity. They found that it evolved 1.717 times as much heat on burning as a gram of sugar.

* Kahlbaums M. B. (unpurified) was used.

The Heats of Combustion of Benzoic Acid, Benzene, Ethyl Propionate, Methyl Butyrate and Methyl - iso - Butyrate (R. & J.)

We now have the ratios of the rise of temperature caused by the combustion of one gram of benzoic acid, benzene, ethyl propionate, methyl butyrate and methyl-iso-butyrate to that caused by one gram of sugar. Let us next determine the heats of combustion of one gram-molecule of these substances.

The following table gives the results obtained:

Substance	Temperature rise per gram of substance / Temperature rise per gram of sugar		Heat of combustion of 1 gram of sugar		Molecular weight of Substance		Molal heat of Combustion
Benzoic Acid	1.6031	x	3945 Cals.	x	122.05	=	771.8 Cals.
Benzene	2.5371		3945		78.05		781.1
Ethyl Propionate	1.7120		3945		120.08		689.4
Methyl Butyrate	1.6096		3945		120.08		648.2
Methyl-iso-Butyrate	1.717		3945		120.08		69122

The Bureau of Standards gave for the molal heat of combustion of benzoic acid the value 7714 Calories per gram. The following are the molal heats of combustion found for benzene by other workers:-

	*Molal heat of combustion of benzene.
Richards, Henderson and Frevert	779.6 Cals.
Richards and Jesse	781.1
Richards and Davis (University of Manitoba)	781.9
Richards and Barry	781.0

The heats of combustion of the three isomeric compounds; ethyl propionate (689.4 Cals.), methyl butyrate (648.2 Cals.), and methyl-iso-butyrate (691.2) indicate that their constitutions have influence on their heats of combustion. In the light of results obtained by previous workers there is not a doubt, however, that the great discrepancy between the heat of combustion of methyl butyrate, and the heats of combustion of ethyl propionate, and methyl-iso-butyrate, is due not to a difference in constitution, but to some other cause, probably impurities in the sample used. This conclusion is further, substantiated by Favre and Silvermann's value for the heat of combustion of methyl butyrate, namely 693.4 Cals., which is quite similar to the heats of combustion of the other two compounds. We intend to further investigate the heats of combustion of these liquids in a purified condition.

Summary

(1) The eficacy of the type of calorimeter used at Cambridge for determining the heats of combustion accurately was further established.

(2) The Standard Calorimeter Bomb was tested and shown to be adaptable for accurate calorimetric determinations.

*Values calculated from their ratios for sugar and benzene, using 3945 Cals. per gram as the heat of combustion of sugar.

(3) Benzoic acid, benzene, ethyl propionate and methyl butyrate were found to evolve respectively at least 1.6031, 2.5371, 1.7120, and 1.6096 times as much heat as an equal weight of sugar on burning.

(4) The heats of combustion of benzoic acid (771.8 Cals.), benzene (781.1 Cals.), ethyl prppionate (689.4 Cals.), and methyl butyrate (648.2 Cals) were determined.

(5) A similarity was shown to exist between the heats of combustion of ethyl propionate, methyl butyrate, and methyl-iso-butyrate (isomers). This, however, was not entirely satisfactory, due to impurity of the liquids.